

CO Hydrogenation: Exploring Iridium as a Promoter for Supported Cobalt Catalysts by TPR-EXAFS/XANES and Reaction Testing

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Abstract The price of iridium currently trends at about half the cost of platinum, the latter being a typical reduction promoter for Co/Al₂O₃ Fischer–Tropsch (FT) synthesis catalysts in gas-to-liquids (GTL) technology. In the current contribution, both fixed-bed catalytic FT and TPR-EXAFS/XANES experiments were carried out over 0.1% iridium-doped 25% Co/Al₂O₃ catalysts in order to (1) assess the effectiveness of Ir as a promoter of cobalt oxide reduction and (2) evaluate the effectiveness of the incipient wetness impregnation (IWI) technique for adding the Ir precursor by comparing a catalyst prepared by IWI to one prepared by atomic layer deposition (ALD). Ir was demonstrated to be an effective promoter for facilitating the second step of cobalt oxide reduction, CoO to Co⁰, and the IWI method was found to be superior to ALD.

Keywords Cobalt · Iridium · Alumina · Incipient wetness impregnation · Atomic layer deposition · TPR · EXAFS · XANES

1 Introduction

The gas-to-liquids (GTL) process relies on the Fischer–Tropsch (FT) synthesis reaction, in which syngas having a

relatively high H₂/CO ratio (~2:1) is converted over a supported cobalt catalysts—usually Co/Al₂O₃—under pressure (e.g., ~20 bar) and mild temperatures (e.g., ~220 °C) to produce a distribution of hydrocarbons—mainly straight chain paraffins—that can be upgraded to transportation fuels (e.g., diesel, jet fuel) [1, 2]. Cobalt catalysts are relatively inactive intrinsically for the water–gas shift reaction, making them good candidates for converting synthesis gas having a high H₂/CO ratio (e.g., derived from natural gas). However, cobalt is more expensive than iron. Thus, catalyst activity must be maintained over long periods of time.

Other factors to consider are particle size and reducibility. Iglesia [3] reported a linear trend between FT activity and cobalt surface area on a per gram of catalyst basis as measured by hydrogen chemisorption, indicating that the active sites for the catalysis are the surface cobalt metal particles. Due to the strong interaction of alumina with cobalt oxides, alumina stabilizes very small cobalt oxide particles. The small particle size is important for producing a significant surface area of metallic cobalt following activation in H₂. However, the highly interacting small particles are difficult to reduce and thus, reduction promoters (e.g., Pt, Ru, and Re) are often employed—and often in combination—to facilitate reduction of the cobalt oxide crystallites to the metallic state.

Reduction of Co₃O₄ clusters takes place in two steps: Co₃O₄ + H₂ → 3CoO + H₂O and then 3CoO + 3H₂ → 3Co⁰ + 3H₂O; this has been recently demonstrated by a TPR-EXAFS/XANES investigation [4]. When the reduction promoter reduces below the reduction temperature of Co₃O₄ to CoO (i.e., which typically occurs in the temperature range of 300–350 °C), as in the case of Pt or Ru [5–8], both steps are typically shifted to lower temperatures.

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However, in the case of Re [5, 9, 10], which reduces at a comparable temperature to the first step of reduction of Co_3O_4 , only the second step of reduction (CoO to Co^0) has been observed to be impacted. Using a standard 10 h H_2 reduction treatment of 350 °C, Jacobs et al. [5] showed by hydrogen chemisorption/pulse reoxidation measurements that in all cases (Pt, Ru, Re), gains in active site densities (i.e., number of cobalt atoms exposed at the surface) were directly due to the higher extents of reduction gained by promoter addition. Two promoters, Pt and Re, have been observed to exhibit direct contact with Co at the atomic level by EXAFS spectroscopy [11–13].

Also, it is evident that not every metal reduction promoter of cobalt oxide displays good activity in the reaction testing. Recently, Jacobs et al. [14] examined Group 11 elements as potential promoters. While Cu, Ag, and Au were found to significantly promote the reduction of cobalt oxides, Cu acted as a poison on the surface of Co. Ag and Au, on the other hand, were able to promote reduction and boost CO conversion levels during FT. Nevertheless, during an EXAFS/XANES investigation comparing freshly reduced catalysts with those obtained by reducing a reduced/passivated catalyst, the Ag and Au catalysts significantly lost their ability to promote reduction after exposure to oxygen. In the initial calcined catalyst, the Ag and Au oxides were initially in good contact with cobalt oxides and during reduction, the tiny Group 11 metal particles formed were able to promote reduction of cobalt. However, after exposure to the 350 °C condition, the promoter agglomerated, disrupting surface contact with cobalt. Thus, once the catalyst was cooled and passivated, it no longer was able to promote reduction a second time.

This contribution examines the possibility of using Ir as a reduction promoter for cobalt alumina catalysts. One reason is that Ir is about one-half the cost of Pt at current prices. The primary aim of the work is to determine, using TPR-EXAFS/XANES, if Ir promotes the reduction of Co_3O_4 to CoO and/or CoO to the Co metal and evaluate differences in cobalt crystallite size following TPR. The second goal is to compare two separate methods of preparation—incipient wetness impregnation (IWI) and atomic layer deposition (ALD)—to gauge the effectiveness of the IWI method against a procedure that is known to effectively produce well-dispersed nanoparticles. Finally, the 0.1% Ir–25% Co/ Al_2O_3 catalysts were tested using a fixed-bed catalytic FT reactor against promoted and unpromoted 25% Co/ Al_2O_3 catalysts to determine if any gains in extent of cobalt reduction led to improved CO conversion rates on a per gram of catalyst basis. This effectively acts as a model reaction to probe the number of Co metal atoms available at the surface.

2 Experimental

2.1 Catalyst Preparation

Catalox SBA150 γ - Al_2O_3 was used as the support for the cobalt FT catalysts. A slurry phase method was used to load cobalt nitrate to the support, such that the loading solution volume was 2.5 times that of the measured pore volume. To obtain a cobalt loading of 25% cobalt, multiple steps were used, due to the limited solubility of the cobalt nitrate salt. Following cobalt addition, the catalyst was dried at 80 and 100 °C in a rotary evaporator following each slurry impregnation. Catalysts were calcined in flowing air at a rate of 1 L/min for 4 h at 350 °C. This sample of 25% Co-catalyst was used in the subsequent experiments in which various promoters were deposited.

IWI was used to prepare samples of iridium and platinum promoted catalysts. Salts of $\text{Ir}(\text{acac})_3$ or $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ were dissolved in sufficient water to wet the above Co-containing catalyst. They were impregnated into the catalyst and subsequently dried and calcined in air at 200 °C for about 1 h after the drying and heat-up stages of about 2 h.

ALD catalysts were prepared using a viscous flow ALD reactor at 1 Torr pressure using ultrahigh purity nitrogen carrier gas. Approximately 0.2 g of the above Co-based catalyst was contained in a fixed bed fixture. This catalyst was treated using alternating exposures to the noble metal precursor and oxygen to deposit ~1 nm nanoparticles. The noble metal precursors for Ir, Pt, and Ru were $\text{Ir}(\text{acac})_3$, $\text{Pt}(\text{MeCp})\text{Me}_3$, and 4-(dimethylpentadienyl)(ethylcyclopentadienyl) ruthenium (DER), respectively. Metal loadings of ~0.1 wt% were achieved by adjusting the deposition temperature in the range 100–300 °C as well as the number of ALD cycles performed. The specific details of the Pt deposition have been described in detail [15]. A similar approach was used to deposit the Ir and Ru.

2.2 TPR-EXAFS/XANES

In situ H_2 -TPR-EXAFS studies were performed at the Materials Research Collaborative Access Team (MR-CAT) beamline at the Advanced Photon Source, Argonne National Laboratory. A cryogenically cooled Si (1 1 1) monochromator selected the incident energy and a rhodium-coated mirror rejected higher order harmonics of the fundamental beam energy. The experiment setup was similar to that outlined by Jacoby [16]. A stainless steel multi-sample holder (3.0 mm i.d. channels) was used to monitor the in situ reduction of 6 samples during a single TPR run. Approximately 6 mg of each sample was loaded as a self-supporting wafer in each channel. The catalyst to diluent weight was approximately 0.1. The holder was

placed in the center of a quartz tube, equipped with gas and thermocouple ports and Kapton windows. The amount of sample used was optimized for the Co K edge, considering the absorption by Al of the support. The quartz tube was placed in a clamshell furnace mounted on the positioning table. Each sample cell was positioned relative to the beam by finely adjusting the position of the table to an accuracy of 20 μm (for repeated scans). Once the sample positions were fine-tuned, the reactor was purged with helium for more than 5 min at 100 mL/min then the reactant gas (H_2/He , 4%) was flowed through the samples (100 mL/min) and a temperature ramp of $\sim 1.5\text{ }^\circ\text{C}/\text{min}$ was initiated for the furnace. A temporary hold of about $\sim 4\text{ h}$ was experienced at a temperature of $500\text{ }^\circ\text{C}$. The Co K-edge spectra were recorded in transmission mode and a Co metallic foil spectrum was measured simultaneously with each sample spectrum for energy calibration. X-ray absorption spectra for each sample were collected from 7,520 to 8,470 eV, with a step size of 0.40 eV and acquisition times of 68 s per sample. By measuring each sample, in turn, and repeating, this allowed 84 scans to be collected for each sample over a

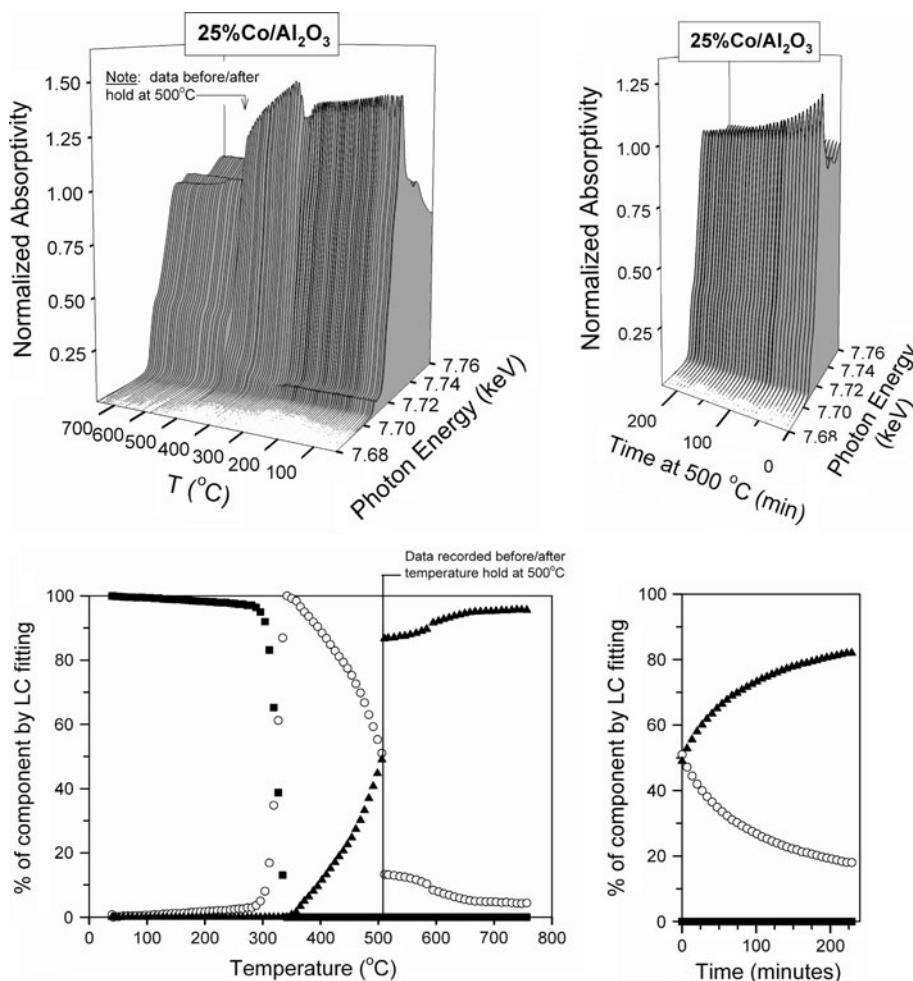
9 h period. The sample's temperature change from the absorption edge through the end of the scan was then about $1.3\text{ }^\circ\text{C}$, while each sample was measured approximately every $10\text{ }^\circ\text{C}$.

Data reduction of the EXAFS/XANES spectra was carried out using the WinXAS program [17]. The details of the XANES and EXAFS analyses are provided in the appendices of our previous article, and will not be repeated here, for the sake of brevity [4]. EXAFS data reduction and fitting were carried out using on the catalysts in their final state following TPR and cooling using the WinXAS [17], atoms [18], FEFF [19], and FEFFIT [20] programs. The k-range used for the fittings was $2\text{--}12\text{ \AA}^{-1}$. Fitting was confined to the first Co-Co metallic coordination shell by applying a Hanning window in the Fourier transform magnitude spectra, and carrying out the back-transform to isolate that shell.

2.3 Reaction Testing

A continuous-flow catalytic-bed unit was used for this FT study. The gaseous feed consisted of 2:1 molar blend

Fig. 1 Hydrogen TPR-XANES profile for the unpromoted 25% Co/ Al_2O_3 catalyst as a function of (top left) temperature and (top right) time at $500\text{ }^\circ\text{C}$. Linear combination fittings as a function of (bottom left) temperature and (bottom right) time are provided



of H₂:CO. The feed passed through a preheater/reactor that consisted of a 1/2-in.-O.D. (3/8-in.-I.D.) tube of 36 in. length. Gaseous flow was downward through the following zones:

- (1) An empty (quartz wool) zone to serve as a preheater,
- (2) Inert packing consisting of low-surface α -Al₂O₃ to ensure radial flow dispersion,
- (3) Supported catalyst that was mixed with inert filler, and
- (4) Additional α -Al₂O₃ packing.

The preheater/reactor had a total of six internal and two external thermocouples. The reactor temperature was controlled using the thermocouple at the center of the active catalyst bed.

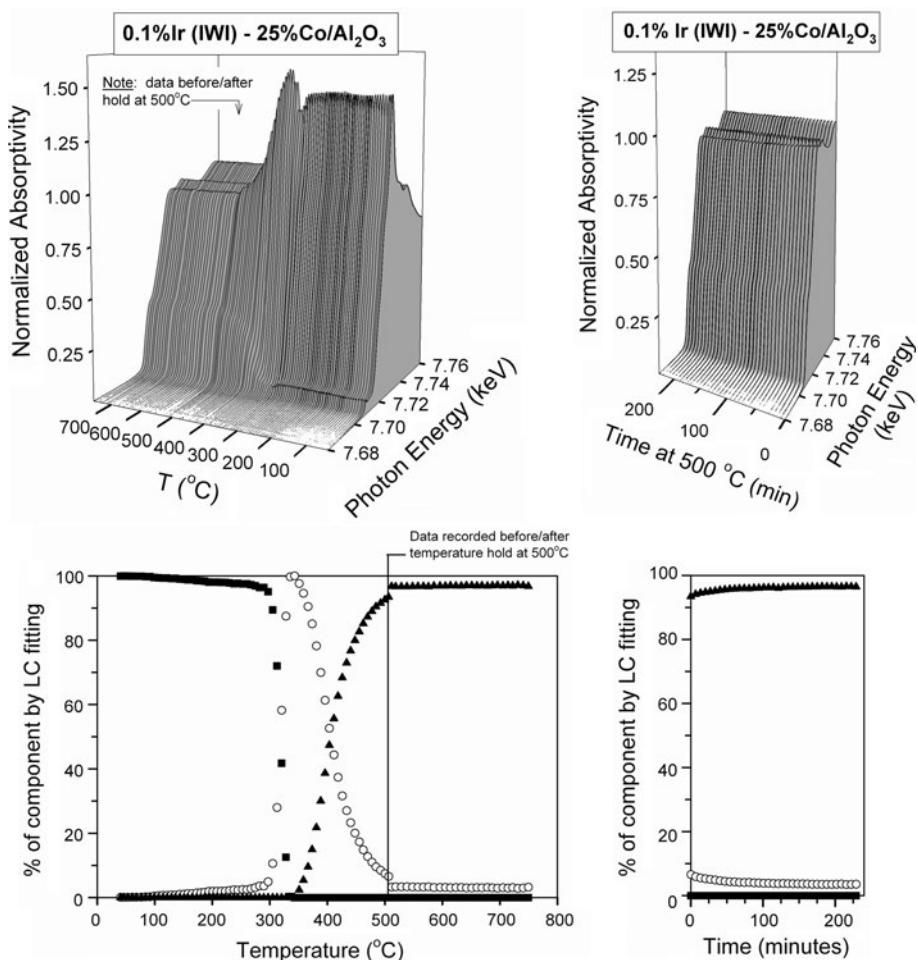
The FT experiments made with particulate catalyst were carried out at temperatures ranging from about 220–300 °C, pressures averaging 13.1 MPa (190 psia), a gas feed rate of about 40 mL/min, and a catalyst charge of 0.1 g. At a gas feed rate of 40 mL/min and a catalyst charge

of 0.1 g, the equivalent space velocity is about 24 normal liters per hour gram (NL/hr g).

The reactor effluent was cooled in air, and the exit gas was passed through a wet-ice-cooled trap. The traps were set up for parallel operation so that periodic condensate samples could be recovered for weighing and sampling. The pressure of the off-gas was controlled, and it was subsequently metered and sampled. The gas composition was determined using an HP 6890 Series gas chromatograph (GC) that had been modified by LINC Quantum Analytics of Foster City, CA. It had three columns: (1) a molecular sieve column (7 ft × 1/16 in. 13 × 45/60) for light gas retention and separation, (2) a capillary column (50 m × 0.53 mm KCl modified Al₂O₃ PLOT) for hydrocarbon analysis by a flame ionization detector (FID), and (3) a packed column (7 ft × 1/16 in. Hayesep A 60/80) for CO₂ separation and analysis using a thermal conductivity detector (TCD).

Catalyst activity is reported in terms of conversion of feed CO to reaction products, namely 100% feed minus products based on a C mass balance.

Fig. 2 Hydrogen TPR-XANES profile for the 0.1% Ir promoted 25% Co/Al₂O₃ catalyst prepared by IWI of Ir as a function of (top left) temperature and (top right) time at 500 °C. Linear combination fittings as a function of (bottom left) temperature and (bottom right) time are provided



3 Results and Discussion

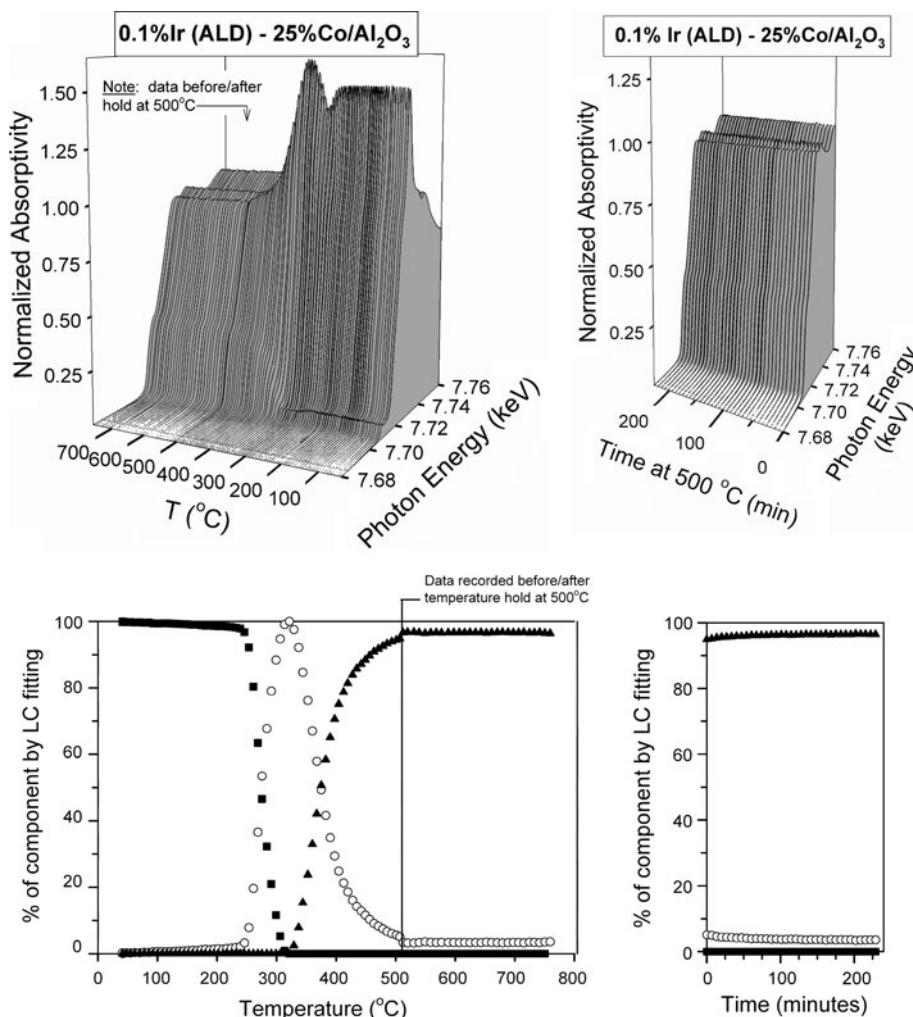
3.1 TPR-EXAFS/XANES Experimentation

TPR-XANES profiles (Figs. 1, 2, 3) in all cases reflect a two-step reduction process [4] for the reduction of Co_3O_4 , whereby the first step, which is completed between 300 and 350 °C is $\text{Co}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{CoO} + \text{H}_2\text{O}$, followed by a second step whereby $\text{CoO} + 3\text{H}_2 \rightarrow 3\text{Co}^0 + 3\text{H}_2\text{O}$. It is clear that even at 750 °C, this step did not achieve complete transformation to Co^0 . Linear combination fitting of spectra with reference compounds suggests that there is a small fraction (typically 5%) that remains oxidized. It may be attributed to residual CoO interacting very strongly with the support or, more likely, to a cobalt-support compound that does not reduce. It is often claimed that a small fraction of cobalt is generally sacrificed to the support as an irreducible cobalt-support compound (e.g., cobalt aluminate). The TPR data of Wang and Chen [21] as a function of cobalt loading on Co/alumina catalysts support this viewpoint.

Examining first the unpromoted 25%Co/ Al_2O_3 catalyst, reduction of Co_3O_4 to CoO is rapid—the catalyst achieves close to 50% conversion of Co_3O_4 to CoO at 322.4 °C and 100% CoO at ~342 °C. Reduction of CoO to Co^0 , the step which generates the active phase for FT, is relatively slower. 50% of the CoO is converted to the metal at ~506 °C.

With incorporation of 0.1% Ir promoter by IWI, the first step of reduction is hardly impacted, with 50% of the Co_3O_4 converting to CoO at 318 °C and 100% CoO at ~343 °C. However, the second reduction step is clearly more rapid, and 50% of the CoO is converted to the metal at 406 °C, which is about 100 °C lower than that of the unpromoted catalyst. This result suggests that Ir oxide itself reduces in the same range of temperature as the first step of cobalt reduction, such that the Ir metal can only facilitate the second step of reduction—one likely possibility being a H_2 dissociation and spillover mechanism, whereby Ir reduces to the metal and facilitates the nucleation of Co^0 within the CoO domains. However, while spillover is an attractive explanation, one cannot rule out the possibility of

Fig. 3 Hydrogen TPR-XANES profile for the 0.1% Ir promoted 25% Co/ Al_2O_3 catalyst prepared by ALD of Ir as a function of (top left) temperature and (top right) time at 500 °C. Linear combination fittings as a function of (bottom left) temperature and (bottom right) time are provided



a direct chemical effect (e.g., from alloying formation) that is responsible for facile reduction.

The addition of 0.1% Ir by atomically dispersed iridium by ALD resulted in measurable decreases in the temperatures required to achieve 50% conversion of Co_3O_4 (~ 274 °C), 100% CoO (322 °C), and 50% transformation of CoO to the metallic Co (374 °C). These later temperatures averaged about 32 °C lower than those generated with the use of IWI Ir.

The TPR-EXAFS results of Figs. 4 and 5 confirm the interpretation of the TPR-XANES data. In all of the TPR-EXAFS spectra, it is evident that cobalt-oxide and cobalt–cobalt coordination reflect Co_3O_4 , and that the oxide converts to a second oxide, CoO, due to the changes in cobalt-oxide and cobalt–cobalt coordination (i.e., between 300 and 350 °C). Finally, only Co–Co coordination of the first coordination shell of metallic cobalt appears at higher temperatures. The more facile reduction of CoO

to Co^0 in the 0.1% Ir-promoted 25% Co/ Al_2O_3 catalyst compared to the unpromoted catalyst is evidenced by the presence and slow loss of the Co–O peak at low atomic distance in the EXAFS spectra plotted of the unpromoted catalyst as a function of time at 500 °C. This peak is absent in the 0.1% Ir-promoted catalysts during the temperature hold at 500 °C.

The reduced catalysts were analyzed following cooling to ambient conditions. According to the Fourier transform magnitude plots (Fig. 6) and the results of EXAFS fittings (Fig. 7; Table 1), there is no measurable difference within experimental error in the coordination number for Co–Co metal that would suggest a significant difference in Co particle size. This result suggests that increases in CO conversion due to gains in Co site densities, are the result of a higher extent of reduction of CoO to Co^0 , the direct result of the role that Ir plays in promoting cobalt oxide reduction.

Fig. 4 Hydrogen TPR-EXAFS profile for the (top) unpromoted 25%Co/ Al_2O_3 catalyst and (bottom) 0.1% Ir promoted 25% Co/ Al_2O_3 catalyst prepared by IWI of Ir as a function of (left) temperature and (right) time at 500 °C

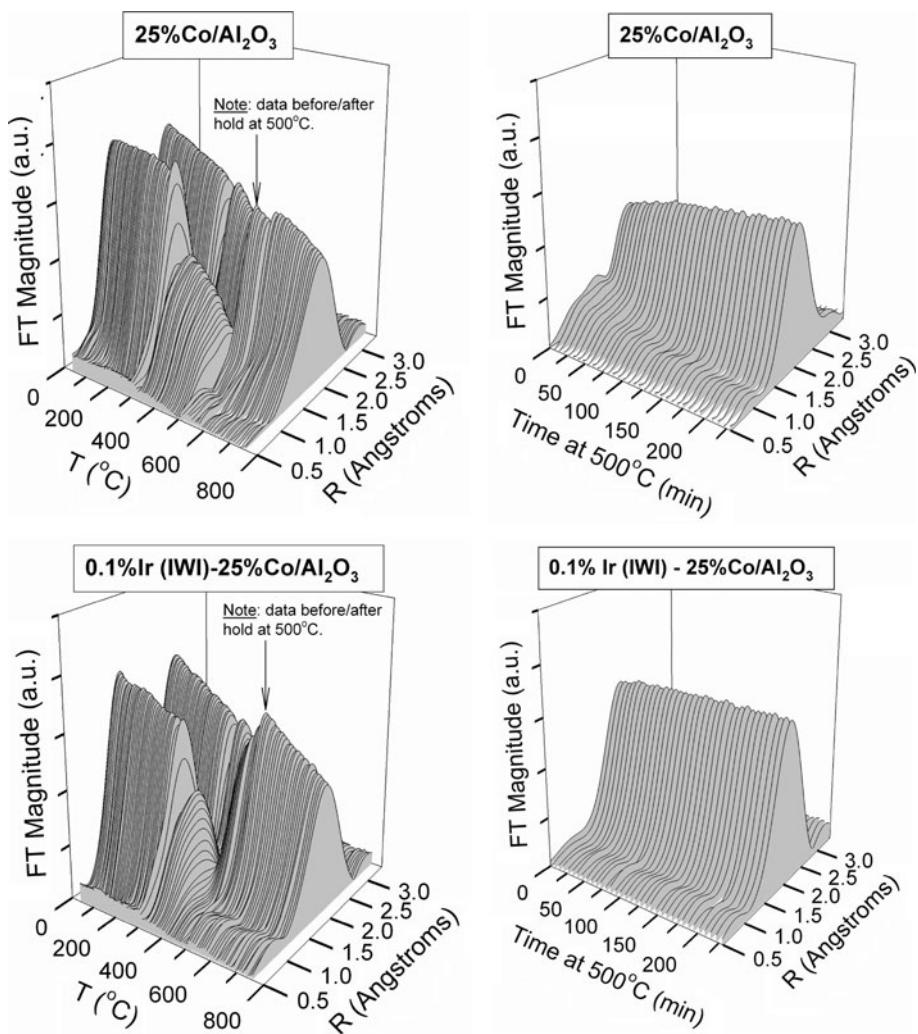


Fig. 5 Hydrogen TPR-EXAFS profile for the 0.1% Ir promoted 25% Co/Al₂O₃ catalyst prepared by ALD of Ir as a function of (left) temperature and (right) time at 500 °C

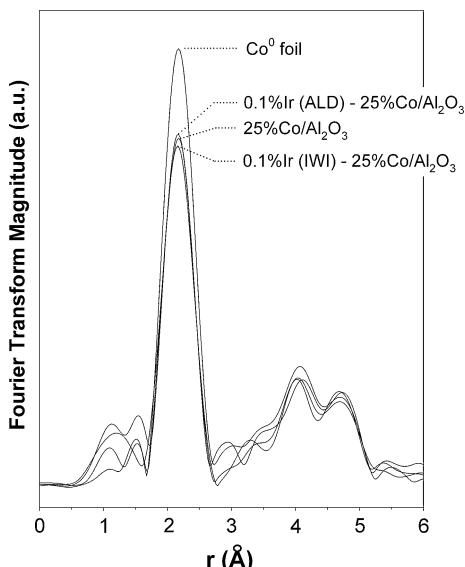
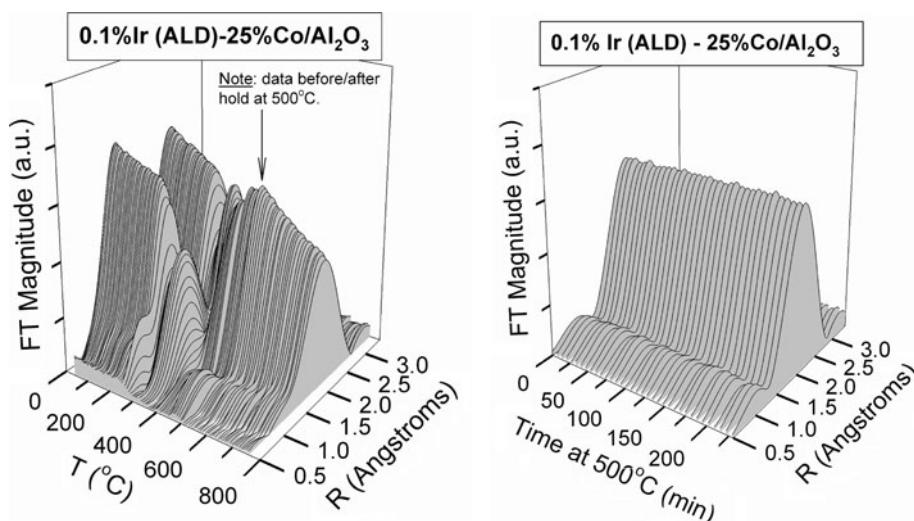


Fig. 6 k^3 -weighted EXAFS Fourier transform magnitude spectra of the supported cobalt catalysts following the hydrogen TPR-EXAFS/XANES experiment and cooling to ambient conditions

3.2 FT Experimentation

Reference FT experiments were carried out using both an empty reactor and one filled with α -Al₂O₃ packing. There was a nominal level of CO conversion presumably due to the presence of a catalytic surface on the thermocouples and stainless steel tubes. To reduce the active catalytic surface effect of the reactor, the stainless tube and associated fittings were coated with alumina using the ALD system. As shown in Fig. 8, there resulted only a nominal conversion of CO to FT hydrocarbons due to reactor surfaces.

As noted in Fig. 8, CO conversion followed a power law correlation with reaction temperature in the range of about

230–280 °C. The base catalyst consisting of 25% Co deposited on Al₂O₃ using the IWI technique. Two experiments made with this later catalyst exhibited reasonable reproducibility.

A comparison of experimental results of catalysts promoted with 0.1% Pt, Ru and Ir is presented in Fig. 8. The use of 0.1% Pt or Ru deposited by the ALD technique as the promoter on 25% Co catalyst increased CO conversion by about 4% at 260 °C; namely 19–23%. The use of the IWI technique to deposit this low level of Pt was shown to be more effective. Specifically, CO conversion was increased from 19% to about 32% again at 260 °C. In the case of depositing Ir on the 25% Co catalyst, the IWI technique was again more effective than that of the ALD technique. At a reaction temperature of 260 °C, the levels of CO conversion were about 33 and 29%, respectively. Overall, the use of Ir as a promoter was more effective than that of either Pt or Ru. However, there remains some question of the difference of activities due to the single result of the IWI Pt observed at about 265 °C.

There also remains the question as to the impact of Ir on the longterm deactivation rate of the catalyst, which is beyond the scope of this work. There has been little work in this area for Ir promoted supported cobalt catalysts. Guczi et al. [22] have argued that Ir may retard the deactivation of Co via H supplied by Ir. Wei et al. [23] tested 0.5% Ir promoted 20% Co catalysts supported on zirconium containing mesoporous silicates and aluminosilicates and, in some cases, found very low deactivation over an approximately 50 h testing period. For example, a catalyst having 0.5% Ir and 20% Co on Zr-MPAS ($Si/(Zr + Al) = 19$, $Zr/Al = 1$) displayed no measurable deactivation over the 50 h run at a conversion level close to 60% at 230 °C, 1 MPa, H₂/CO of 2:1, and W/F = 10 g catalyst h mol⁻¹. Okabe et al. [24] also obtained catalysts with good

Fig. 7 k^3 -weighted EXAFS Fourier transform magnitude spectra after the TPR experiment after catalysts were cooled to close to ambient conditions: (left) unfiltered k^3 -weighted $\chi(k)$ spectra; (middle) k^3 -weighted Fourier transform magnitude spectra (solid line) and resulting fitting (filled circles) over the first Co–Co coordination shell; and (right) filtered k^3 -weighted $\chi(k)$ spectra (solid line) and result of fitting (filled circles)

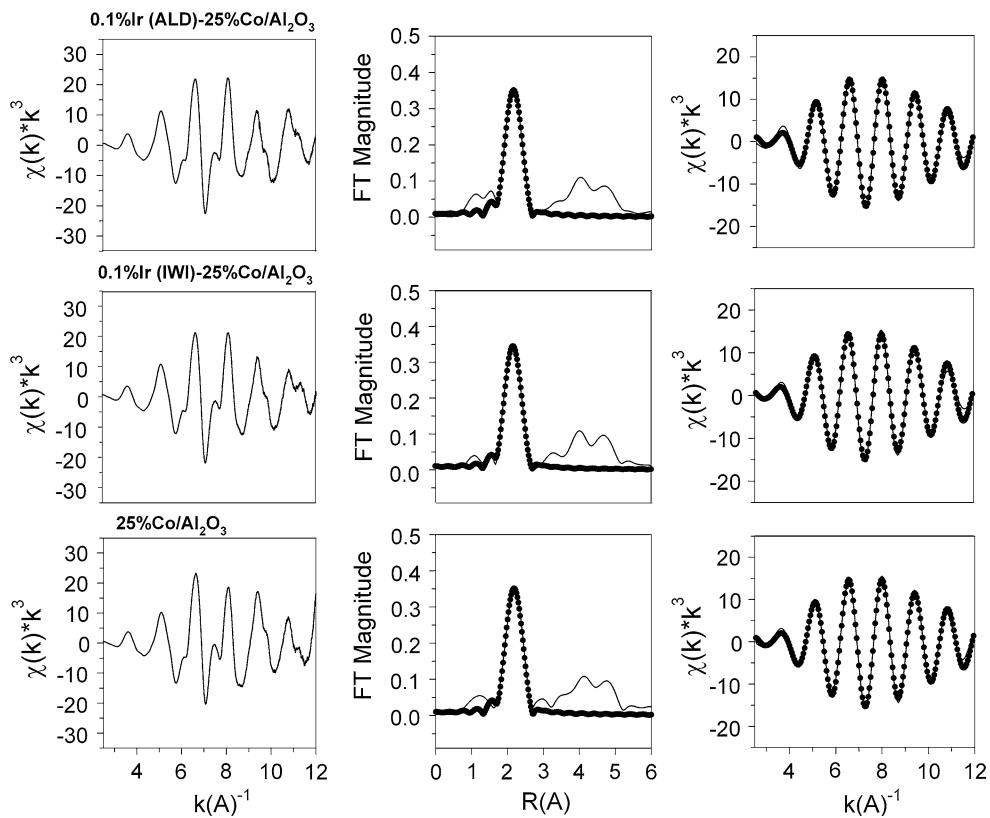


Table 1 EXAFS Co–Co first Co^0 coordination shell fitting parameters for catalysts cooled to ambient conditions after TPR

Catalyst	n	Δn	S_0^2	e_0 (eV)	Δe_0 (eV)	R (Å)	ΔR (Å)	σ^2 (Å) ²	$\Delta \sigma^2$ (Å) ²	r factor
Co ⁰ foil	12.0	—	0.90	7.4	1.5	2.494	0.008	0.0078	0.0004	0.013
25% Co/Al ₂ O ₃	8.9	0.2	0.90	7.8	0.7	2.500	0.004	—	—	0.0025
0.1% Ir (IWI)-25% Co/Al ₂ O ₃	8.7	0.3	0.90	6.2	1.2	2.488	0.006	—	—	0.007
0.1% Ir (ALD)-25% Co/Al ₂ O ₃	8.8	0.3	0.90	7.4	1.0	2.496	0.005	—	—	0.0047

Note: set parameters in bold text

stability in runs lasting up to 100 h over bimodal Co–Ir/SiO₂ catalysts prepared by an alkoxide method. The conversion level was close to 60% and the conditions were virtually identical to those used by Wei et al. [23]. Thus, although longterm deactivation data in the literature is lacking for the cobalt iridium system, the available stability data looks promising.

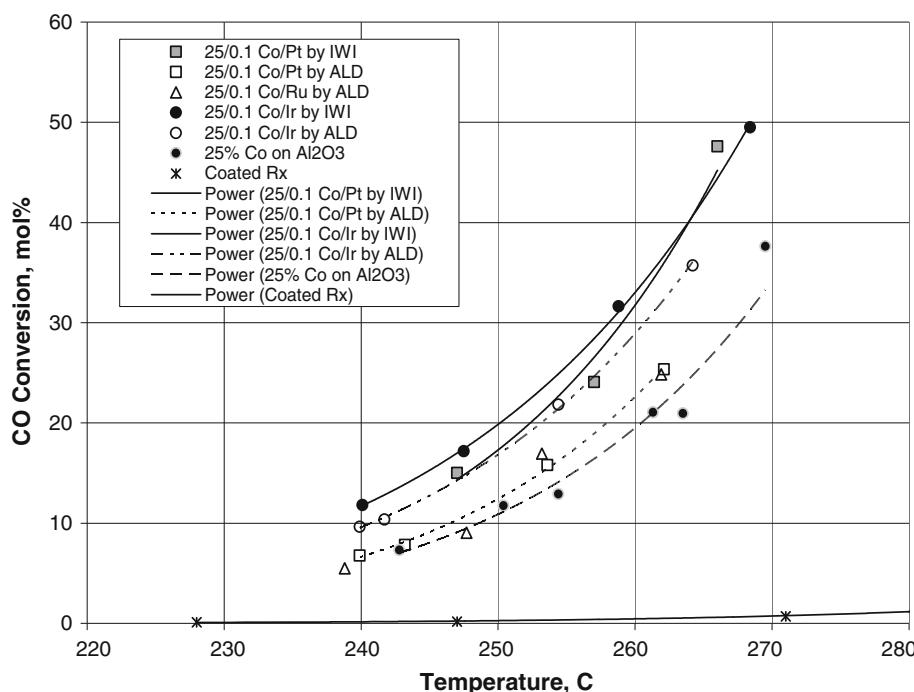
The apparent superiority of the IWI technique to the ALD technique in this work may result from lower-than-expected noble metal loadings on the ALD catalysts. These metal loadings were estimated based on the known ALD growth rates for these materials in the steady-state (metal growth on a metal surface). However, the initial substrate surface can influence the ALD growth rate in the early stages of deposition. A more precise determination of the metal loadings for the IWI and ALD

catalysts using ICP measurements could resolve these uncertainties.

4 Conclusions

Both FT synthesis and TPR-EXAFS/XANES experiments were carried out over 0.1% iridium-doped 25% Co/Al₂O₃. Both approaches demonstrated that Ir was an effective promoter for improving the effectiveness of Co-containing FT catalysts. Specifically, Ir facilitated the second step of cobalt oxide reduction, CoO to Co⁰; thereby, reducing the needed temperature for the pre-treatment (reduction with hydrogen) of the FT catalyst. It was also demonstrated that the IWI method was found to be nominally superior to that of the ALD technique.

Fig. 8 Comparison of the effects of various promoters with 0.1% deposited on 25% Co reference catalysts (400 °C reduction; 0.1 g catalyst charge)



Based upon the FT experimental results, the use of Ir as a promoter is nominally superior to Pt and significantly better than Ru.

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